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ning of each regular issue of the PCT Gazette.

(54) Title: POLYETHYLENE MOLDING COMPOSITION FOR COATING STEEL PIPES

(57) Abstract: The invention relates to a polyethylene molding composition which has a multimodal molar mass distribution and is particularly suitable for producing protective coatings on steel pipes. The molding composition has a density at a temperature of 23°C in the range from 0.94 to 0.95 g/cm³ and An MFI_{190/5} in the range from 1.2 to 2.1 dg/min. It comprises from 45 to 55% by weight of a low molecular weight ethylene homopolymer A, from 30 to 40% by weight of a high molecular weight copolymer B of ethylene and another olefin having from 4 to 8 carbon atoms and from 10 to 20% by weight of an ultra high molecular weight ethylene copolymer C.



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Title: Polyethylene molding composition for coating steel pipes

5 The present invention relates to a polyethylene molding composition which has a multimodal molar mass distribution and is particularly suitable for producing protective coatings on pipes, and a process for preparing this molding composition in the presence of a catalytic system comprising a Ziegler
10 catalyst and a cocatalyst via a multistage reaction sequence comprising successive polymerization steps.

Polyethylene is widely used for industrial applications in which a material having a high mechanical strength and a high
15 resistance to thermooxidative degradation is required in order to ensure a long life even at elevated use temperatures. For this application, it is also advantageous for the polyethylene molding composition to have a low permeability to water vapor and oxygen because the steel pipe is then effectively
20 protected against corrosion by moisture and contact with air. In addition, polyethylene has the particular advantages that it has good chemical resistance, it has a low intrinsic weight and it is a material which can easily be processed in the melt.

25 WO 97/03139 describes a coating composition based on polyethylene which has a bimodal molar mass distribution, are suitable for producing coatings on metal pipes and give the coated substrate improved durability in respect of corrosion,
30 in respect of oxidative aging, in respect of weathering influences of all types and in respect of mechanical stresses.

Known polyethylene molding compositions having a unimodal molar mass distribution have disadvantages in terms of their
35 processability, their environmental stress cracking resistance

and their mechanical toughness. Compared to these, molding compositions having a bimodal molar mass distribution represent a technical improvement. They are easier to process and have (as indicated by the density) an improved
5 stiffness/environmental stress cracking resistance ratio.

It was thus an object of the present invention to develop a polyethylene molding composition which retains good processability but displays significant advantages in respect
10 of environmental stress cracking resistance and resistance to mechanical stresses, in particular at temperatures below 0°C.

This object is achieved by a molding composition of the generic type mentioned at the outset whose distinguishing
15 features are that it comprises from 45 to 55% by weight of a low molecular weight ethylene homopolymer A, from 30 to 40% by weight of a high molecular weight copolymer B of ethylene and another olefin having from 4 to 8 carbon atoms and from 10 to 20% by weight of an ultra high molecular weight ethylene
20 copolymer C, where all percentages are based on the total weight of the molding composition.

The invention further provides a process for preparing this molding composition in a cascaded suspension polymerization
25 and a defect-free coating of steel pipes comprising this molding composition and having excellent mechanical strength properties combined with high stiffness.

The polyethylene molding composition of the invention has a
30 density at a temperature of 23°C in the range from 0.94 to 0.95 g/cm³ and a broad trimodal molar mass distribution. The high molecular weight copolymer B contains a proportion of further olefin monomer units having from 4 to 8 carbon atoms, namely from 5 to 8% by weight. Examples of such comonomers are
35 1-butene, 1-pentene, 1-hexene, 1-octene and 4-methyl-1-

pentene. The ultra high molecular weight ethylene copolymer C likewise contains one or more of the abovementioned comonomers in an amount in the range from 7 to 11% by weight.

- 5 Furthermore, the molding composition of the invention has a melt flow index in accordance with ISO 1133, expressed as $MFI_{190/5}$, in the range from 1.2 to 2.1 dg/min and a viscosity number $VN_{overall}$, measured in accordance with ISO/R 1191 in decalin at a temperature of 135°C, in the range from 260 to
10 340 cm^3/g , in particular from 280 to 320 cm^3/g .

The trimodality as a measure of the position of the centers of gravity of the three individual molar mass distributions can be described with the aid of the viscosity numbers VN in
15 accordance with ISO/R 1191 of the polymers formed in the successive polymerization stages. Here, the band widths of the polymers formed in the individual reaction stages are as follows:

- 20 The viscosity number VN_1 measured on the polymer after the first polymerization stage is identical to the viscosity number VN_A of the low molecular weight polyethylene A and is, according to the invention, in the range from 70 to 90 cm^3/g .
- 25 The viscosity number VN_2 measured on the polymer after the second polymerization stage does not correspond to VN_B of the relatively high molecular weight polyethylene B formed in the second polymerization stage, which can be determined only mathematically but is instead the viscosity number of the
30 mixture of polymer A plus polymer B. According to the invention, VN_2 is in the range from 150 to 180 cm^3/g .

The viscosity number VN_3 measured on the polymer after the third polymerization stage does not correspond to VN_C of the
35 ultra high molecular weight copolymer C formed in the third

polymerization stage, which can likewise be determined only mathematically, but is instead the viscosity number of the mixture of the polymer A, polymer B plus polymer C. According to the invention, VN_3 is in the range from 260 to 340 cm^3/g , in particular from 280 to 320 cm^3/g .

The polyethylene is obtained by polymerization of the monomers in suspension at temperatures in the range from 70 to 90°C, preferably from 80 to 90°C, a pressure in the range from 2 to 10 bar and in the presence of a highly active Ziegler catalyst composed of a transition metal compound and an organoaluminum compound. The polymerization is a three-stage polymerization, i.e. it is carried out in three successive stages, with the molar mass being regulated in each stage by means of added hydrogen.

Apart from the polyethylene, the polyethylene molding composition of the invention can further comprise additional additives. Such additives are, for example, heat stabilizers, antioxidants, UV absorbers, light stabilizers, metal deactivators, peroxide-decomposing compounds, basic costabilizers, in amounts of from 0 to 10% by weight, preferably from 0 to 5% by weight, and also fillers, reinforcing materials, plasticizers, lubricants, emulsifiers, pigments, optical brighteners, flame retardants, antistatics blowing agents, or combinations of these in total amounts of from 0 to 50% by weight, based on the total weight of the mixture.

The molding composition of the invention is particularly useful for producing coatings on metal pipes by extrusion by firstly plasticizing the polyethylene molding composition in an extruder at temperatures in the range from 200 to 250°C and then extruding it through a suitable nozzle onto the pipe surface and cooling it there.

The molding composition of the invention can be processed particularly well by the extrusion process to produce coatings because it has a notched impact toughness (ISO) in the range
5 from 8 to 14 kJ/m² and an environmental stress cracking resistance (ESCR) in the range > 200 h.

The notched impact toughness_{ISO} is measured at -30°C in accordance with ISO 179-1/1eA / DIN 53453. The dimensions of
10 the specimen are 10 x 4 x 80 mm, and it is provided with a V-notch having an angle of 45°, a depth of 2 mm and a radius at the bottom of the notch of 0.25 mm.

The environmental stress cracking resistance (ESCR) of the
15 molding composition of the invention is determined by an internal measurement method and is reported in h. This laboratory method is described by M. Fleißner in Kunststoffe 77 (1987), p. 45 ff, and corresponds to ISO/CD 16770 which is now valid. The publication shows that there is a relationship
20 between the determination of slow crack growth in a creep test on test rods having a circumferential notch and the brittle branch of the internal pressure test in accordance with ISO 1167. A shortening of the time to failure is achieved by shortening the crack initiation time by means of the notch
25 (1.6 mm/razor blade) in ethylene glycol as medium inducing environmental stress cracking at a temperature of 80°C and a tensile stress of 3.5 MPa. The production of the specimens is carried out by sawing three test specimens having dimensions of 10 x 10 x 90 mm from a 10 mm thick pressed plate. The test
30 specimens are in turn notched in the middle by means of a razor blade in a notching apparatus made in-house for this purpose (cf. figure 5 in the publication). The notch depth is 1.6 mm.

Example 1

The polymerization of ethylene was carried out in a continuous process in three reactors connected in series. A Ziegler catalyst which had been prepared by the method of WO 91/18934, example 2, and has the operations number 2.2 in the WO in an amount of 0.08 mmol/h and also sufficient suspension medium (hexane), triethylaluminum as cocatalyst in an amount of 0.08 mmol/h, ethylene and hydrogen were fed into the first reactor. The amount of ethylene (= 65 kg/h) and the amount of hydrogen (= 68 g/h) were set so that a proportion of from 25 to 26% by volume ethylene and a proportion of 65% by volume of hydrogen were measured in the gas space of the first reactor; the remainder was a mixture of nitrogen and vaporized suspension medium.

The polymerization in the first reactor was carried out at a temperature of 84°C.

The suspension from the first reactor was then passed to a second reactor in which the proportion of hydrogen in the gas space had been reduced to 7 - 9% by volume and into which an amount of 48.1 kg/h of ethylene plus an amount of 2940 g/h of 1-butene were introduced. The reduction in the amount of hydrogen was achieved by means of H₂ intermediate depressurization. 73% by volume of ethylene, 8% by volume of hydrogen and 0.82% by volume of 1-butene were measured in the gas space of the second reactor; the remainder was a mixture of nitrogen and vaporized suspension medium. Additionally suspension medium and triethylaluminum were introduced.

The polymerization in the second reactor was carried out at a temperature of 83°C.

The suspension from the second reactor was passed via a further H₂ intermediate depressurization, by means of which the amount of hydrogen in the gas space in the third reactor was set to 2.5% by volume, into the third reactor.

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An amount of 16.9 kg/h of ethylene plus an amount of 1500 g/h of 1-butene were introduced into the third reactor. A proportion of ethylene of 87% by volume, a proportion of hydrogen of 2.5% by volume and a proportion of 1-butene of 1.2% by volume were measured in the gas space of the third reactor; the remainder was a mixture of nitrogen and vaporized suspension medium. In addition, suspension medium and triethylaluminum were introduced.

10

15 The polymerization in the third reactor was carried out at a temperature of 83°C.

20

The long-term activity of the polymerization catalyst necessary for the above-described cascaded mode of operation was ensured by a specially developed Ziegler catalyst having the composition reported in the WO document mentioned at the outset. A measure of the usability of this catalyst is its extremely high response to hydrogen and its high activity which remains constant over a long period of from 1 to

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8 hours.

The suspension medium is separated off from the polymer suspension leaving the third reactor, the powder is dried and the powder is passed to pelletization.

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The viscosity numbers and the proportions W_A , W_B and W_C of polymers A, B and C for the polyethylene molding composition prepared as described in example 1 are shown in table 1 below.

35

Example	1
W _A [% by weight]	50
W _B [% by weight]	37
W _C [% by weight]	13
VN ₁ [cm ³ /g]	80
VN ₂ [cm ³ /g]	165
VN _{overall} [cm ³ /g]	304
FNCT [h]	220
AFM (-30°C)	3.8 kJ/m ²
ACN (+23°C)	13 kJ/m ²

The abbreviations for the physical properties in table 1 have the following meaning:

5

- FNCT = environmental stress cracking resistance (Full Notch Creep Test) measured by the internal measurement method described by M. Fleißner in [h], conditions: 95°C, 3.5 MPa, water / 2% of Arkopal.

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- AFM (-30°C) = notched impact toughness, measured in accordance with ISO 179-1/1eA / DIN 53453 in [kJ/m²] at -30°C.

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- ACN (+23°C) = notched impact toughness, measured in accordance with ISO 179-1/1eA / DIN 53453 in [kJ/m²] at +23°C.

20

Claims

1. A polyethylene molding composition which has a multimodal molar mass distribution and has a density at a temperature of 23°C in the range from 0.94 to 0.95 g/cm³ and an MFI_{190/5} in the range from 1.2 to 2.1 dg/min and comprises from 45 to 55% by weight of a low molecular weight ethylene homopolymer A, from 30 to 40% by weight of a high molecular weight copolymer B of ethylene and another olefin having from 4 to 8 carbon atoms and from 10 to 20% by weight of an ultra high molecular weight ethylene copolymer C, where all percentages are based on the total weight of the molding composition.
2. The polyethylene molding composition according to claim 1, wherein the high molecular weight copolymer B contains from 5 to 8% by weight, based on the weight of copolymer B, of comonomers having from 4 to 8 carbon atoms and the ultra high molecular weight ethylene copolymer C contains from 7 to 11% by weight, based on the weight of copolymer C, of comonomers.
3. The polyethylene molding composition according to claim 1 or 2 in which 1-butene, 1-pentene, 1-hexene, 1-octene, 4-methyl-1-pentene or mixtures thereof are present as comonomers.
4. The polyethylene molding composition according to one or more of claims 1 to 3 which has a viscosity number VN_{overall}, measured in accordance with ISO/R 1191 in decalin at a temperature of 135°C in the range from 260 to 340 cm³/g, preferably from 280 to 320 cm³/g.
5. The polyethylene molding composition according to one or more of claims 1 to 4 which has a notched impact toughness

AFM (-30°C) in the range from 3.5 to 4.5 kJ/m² and a notched impact toughness ACN ($+23^{\circ}\text{C}$) in the range from 12 to 16 kJ/m² and has an environmental stress cracking resistance (FNCT) in the range from 150 to 250 h.

5

6. A process for preparing a polyethylene molding composition according to one or more of claims 1 to 5, in which the polymerization of the monomer is carried out in suspension at temperatures in the range from 20 to 120°C, a pressure in the range from 2 to 10 bar and in the presence of a highly active Ziegler catalyst composed of a transition metal compound and an organoaluminum compound, wherein the polymerization is a three-stage polymerization, with the molar mass of the polyethylene formed in each stage being regulated in each case by means of hydrogen.

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7. The process according to claim 6, wherein the hydrogen concentration in the first polymerization stage is set so that the viscosity number VN₁ of the low molecular weight polyethylene A is in the range from 70 to 90 cm³/g.

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8. The process according to claim 6 or 7, wherein the hydrogen concentration in the second polymerization stage is set so that the viscosity number VN₂ of the mixture of polymer A plus polymer B is in the range from 150 to 180 cm³/g.

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9. The process according to any of claims 6 to 8, wherein the hydrogen concentration in the third polymerization stage is set so that the viscosity number VN₃ of the mixture of polymer A, polymer B plus polymer C is in the range from 260 to 340 cm³/g, in particular from 280 to 320 cm³/g.

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10. The use of a polyethylene molding composition according to one or more of claims 1 to 5 for producing protective

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coatings on steel pipes, wherein the polyethylene molding composition is firstly plasticized in an extruder at temperatures in the range from 200 to 250°C and is then extruded through a nozzle onto the surface of the pipe and is cooled there.

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A. CLASSIFICATION OF SUBJECT MATTER
C08F297/08 C08L23/06 C08L23/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

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C08F C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2004/058876 A (BASELL POLYOLEFINE GMBH; BERTHOLD, JOACHIM; BOEHM, LUDWIG; KRUEMPEL, P) 15 July 2004 (2004-07-15) the whole document	1-10
A	WO 2004/058878 A (BASELL POLYOLEFINE GMBH; BERTHOLD, JOACHIM; BOEHM, LUDWIG; KRUEMPEL, P) 15 July 2004 (2004-07-15) the whole document	1-10
A	WO 2004/058877 A (BASELL POLYOLEFINE GMBH; BERTHOLD, JOACHIM; BOEHM, LUDWIG; KRUEMPEL, P) 15 July 2004 (2004-07-15) the whole document	1-10
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2004/056921 A (BASELL POLYOLEFINE GMBH; BERTHOLD, JOACHIM; BOEHM, LUDWIG; KRUEMPEL, P) 8 July 2004 (2004-07-08) the whole document -----	1-10
A	US 6 713 561 B1 (BERTHOLD JOACHIM ET AL) 30 March 2004 (2004-03-30) the whole document -----	1-10
A	US 4 336 352 A (SAKURAI ET AL) 22 June 1982 (1982-06-22) the whole document -----	1-10
A	US 4 536 550 A (MORIGUCHI ET AL) 20 August 1985 (1985-08-20) the whole document -----	1-10

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 2004058876	A	15-07-2004	AU 2003293791 A1	22-07-2004
			BR 0317322 A	08-11-2005
			CA 2511358 A1	15-07-2004
			EP 1578862 A1	28-09-2005
WO 2004058878	A	15-07-2004	AU 2003293815 A1	22-07-2004
			BR 0317343 A	08-11-2005
			CA 2511547 A1	15-07-2004
			EP 1576048 A1	21-09-2005
WO 2004058877	A	15-07-2004	AU 2003296630 A1	22-07-2004
			BR 0317320 A	08-11-2005
			CA 2511545 A1	15-07-2004
			EP 1576049 A1	21-09-2005
WO 2004056921	A	08-07-2004	AU 2003293792 A1	14-07-2004
			BR 0316920 A	25-10-2005
			CA 2510063 A1	08-07-2004
			EP 1576047 A1	21-09-2005
US 6713561	B1	30-03-2004	AT 244264 T	15-07-2003
			AU 769434 B2	29-01-2004
			AU 7001700 A	30-04-2001
			BR 0014232 A	04-06-2002
			CA 2387708 A1	05-04-2001
			CN 1376170 A	23-10-2002
			DE 19945980 A1	29-03-2001
			WO 0123446 A1	05-04-2001
			EP 1228101 A1	07-08-2002
			ES 2200919 T3	16-03-2004
			JP 2003510429 T	18-03-2003
			ZA 200202267 A	15-10-2003
US 4336352	A	22-06-1982	BE 884866 A1	16-12-1980
			BR 8005307 A	04-03-1981
			CA 1138148 A1	21-12-1982
			DE 3031540 A1	09-04-1981
			FR 2463791 A1	27-02-1981
			GB 2056996 A	25-03-1981
			IT 1193551 B	08-07-1988
			JP 1282819 C	27-09-1985
			JP 56032506 A	02-04-1981
			JP 59010724 B	10-03-1984
			NL 8004745 A	26-02-1981
US 4536550	A	20-08-1985	CA 1218181 A1	17-02-1987
			DE 3470168 D1	05-05-1988
			EP 0129312 A1	27-12-1984